

How can computer simulations contribute to the understanding of the dynamics of glasses and glass melts? *

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Introduction

Ever since it became possible to perform computer simulations of systems with a few hundred particles this method was also used to investigate the structure and dynamics of supercooled liquids and glasses. The absence of long range order makes these systems a very difficult task for any sort of analytical calculations and since experiments often cannot give all the desired information, be it of structural or dynamical nature, computer simulations offer a very convenient way to access such information. The goal of the present article is to review some exemplary results of investigations in which the dynamics of supercooled liquids was studied. In this we will focus on recent studies of the prototypical network glassformer SiO_2 , since the lack of space does not permit us to review the large body of literature which exists on the general subject of computer simulations of supercooled liquids and glasses. However, the interested reader can find a more thorough discussion of this subject in the review articles [1, 2, 3, 4].

Before we start to introduce the model we used in our simulations and to present the results, we briefly discuss what the kind of questions are that can be addressed by means

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of computer simulations. Although it is of course *in principle* possible to make a full scale *ab initio* simulation of any given material, the computational demand restricts such types of investigations to systems that are relatively small (less than 100 particles) and to short times (on the order of 10ps). Such system sizes and time scales are for most applications in the field of glasses too small/short and thus one usually limits oneself to simulations in which the system is described by a classical force field. However, it is essentially impossible to devise classical force fields that reproduce exactly the forces in the real material and in practice thus one always uses some approximative potentials. Therefore it is clear that it is most improbable that any simulation will reproduce *all* experimentally determined quantities (density, bond-angles, viscosity, density of states, etc.). In Ref. [5], e.g., it is nicely demonstrated how various potentials for SiO_2 can give very different answers regarding the absolute numbers of various physical quantities, such as the temperature at which the model shows a maximum in the density or on the temperature dependence of the diffusion constant, but the bottom line is that most reasonable potentials agree at least qualitatively with the experimental findings. Thus, if the potential model is sufficiently realistic it can be expected that such a simulation will reproduce at least the salient features of the material and that therefore one can use the simulation to identify trends (e.g., temperature dependence of the density) or mechanisms (e.g., diffusion mechanism) that are present in the real material as well.

Despite the fact that usually one does not demand a *perfect* agreement between the results of a simulation and real experiments, it is often not a simple task to find a potential which gives at least a fair agreement. An example for this situation is B_2O_3 for which it seems to be quite difficult to come up with a good classical potential [6]. Thus it is quite often the case that the main obstacle to use computer simulations in order to gain insight into the properties of supercooled liquids and glasses are not the lack of computational resources but the shortage of classical force fields that give a realistic description of the real material. Therefore it would be most useful if progress would be made in the development of classical force fields.

Model and Details of the Simulation

In this section we present the model we used for our SiO_2 simulation and discuss some of the technical details of the simulation. More details can be found in Refs. [7, 8, 9, 10].

A few years ago *van Beest et al.* introduced a model for SiO_2 in which the interactions

between the ions are of a pure two-body type [11]. Despite the absence of three-body interactions this model is able to generate the tetrahedral network of silica which is thought to give the correct local structure of this system. It was subsequently shown that this potential gives a good description of the various crystalline phases of silica [12] and of the *static* properties of amorphous SiO₂ as well [13, 14]. Thus it is reasonable to use this potential also to investigate the *dynamical* properties of supercooled silica. The potential energy between two ions of type i and j ($i, j \in \{\text{Si}, \text{O}\}$), a distance r_{ij} apart, are given by

$$\phi(r_{ij}) = \frac{q_i q_j e^2}{r_{ij}} + A_{ij} e^{-B_{ij} r_{ij}} - \frac{C_{ij}}{r_{ij}^6} \quad . \quad (1)$$

The values of the parameters q_i , A_{ij} , B_{ij} and C_{ij} can be found in the original publication [11]. The non-Coulombic part of the potential was truncated and shifted at 5.5Å. The simulations were done at constant volume and the density of the system was fixed to 2.37 g/cm³. The system size was 8016 ions, giving a volume of the cubic box of (48.37Å)³. This size is significantly larger than the ones commonly used in such simulations but necessary in order to avoid finite size effects which have been shown to be remarkably pronounced in network glassformers [7]. The equations of motion were integrated with a time step of 1.6 fs. The temperatures investigated were 6100 K, 5200 K, 4700 K, 4300 K, 4000 K, 3760 K, 3580 K, 3400 K, 3250 K, 3100 K, 3000 K, 2900 K and 2750 K. At all temperatures the length of the runs were longer than the typical relaxation time of the system and extended at the lowest temperature over about 20 ns. More details on the simulations can be found in Ref. [10].

Results

One of the simplest dynamical quantities that can be obtained from a computer simulation is the diffusion constant D of a tagged particle, which can be computed from the long time behavior of the mean squared displacement. Care has to be taken, however, that D is determined from a time window in which the mean squared displacement has indeed reached its asymptotic time dependence, i.e. shows a t^1 dependence. Otherwise the computed value of D will be too large.

In Fig. 1 we show the temperature dependence of D_{Si} and D_{O} , the self diffusion constant for the silicon and oxygen atoms, respectively. We see that for all temperatures investigated D_{O} is larger than D_{Si} , which is to be expected since the oxygen atoms are, on average, bound to the network by only two covalent bonds, whereas the silicon atoms are

bound by four bonds. For low temperatures the diffusion constants show the Arrhenius temperature dependence well known from experiments. The two straight lines are an Arrhenius fit to the low temperature data with activation energies of 4.66eV and 5.18eV for the oxygen and silicon atoms, respectively. These values agree well with the experimental values determined by *Mikkelsen* [15] and *Brébec et al.* [16], see figure, and thus we conclude that the used model for SiO₂ is indeed able to give a quite realistic description of the dynamics of supercooled silica. (We note that there is some evidence that for the model of van Beest *et al.* the activation energy for silicon might, at low temperatures, be even a bit larger than the value obtained from the presented fit [10].) From the figure we also recognize that at higher temperatures the diffusion constants deviate from the Arrhenius behavior observed at low temperatures in that they are smaller than expected from an extrapolation with the Arrhenius law. So far this behavior has not been observed in real experiments, since the temperatures accessed so far in the experiments are still a bit lower than the ones for which the non-Arrhenius behavior is observed. But of course we cannot exclude the possibility that the observed non-Arrhenius behavior is an artifact of the used potential with no counterpart in the real material. On the other hand, the investigation of *Hemmati et al.* has shown that many silica models show such a non-Arrhenius behavior, although at different temperatures, thus giving support to the expectation that also real silica will show this behavior at sufficiently high temperatures.

In order to gain some insight why at high temperatures the temperature dependence of the diffusion constants seems to be different from the one at low temperatures, we can study the dynamics of the particles in more detail. This can be done with the help of the self part of the van Hove correlation function which is defined as [17]

$$G_s^{(\alpha)}(r, t) = \frac{1}{N_\alpha} \left\langle \sum_{i=1}^{N_\alpha} \delta(r - |\vec{r}_i(t) - \vec{r}_i(0)|) \right\rangle, \alpha \in \{\text{Si}, \text{O}\} \quad . \quad (2)$$

Here $\langle . \rangle$ stands for the thermal average. Thus $G_s^{(\alpha)}(r, t)$ is the probability that a particle of type α has moved within time t a distance r . In Fig. 2 we show $4\pi r^2 G_s^{(\text{O})}(r, t)$ versus r for different times. From these figures we recognize that at high temperatures, Fig. 2a, the function is a single peaked function with a maximum that is moving to larger values of r when time increases. With decreasing temperature the speed with which the peak moves to larger distances decreases, but qualitatively the shape of the curves is similar to the ones shown in Fig. 2a. This behavior is very similar to the one observed for *fragile* glassformers [2, 3], where at low temperatures the dynamics of the particles is described

very well by the so-called mode-coupling theory [18, 19], which predicts such a time and space dependence of $G_s(r, t)$. If the temperature is lowered further, say below 3500 K, this qualitative picture changes, in that for intermediate times $G_s(r, t)$ shows a double peak structure, see the curve for $t = 4.5$ ns in Fig. 2b. This secondary maximum, marked by an arrow, is usually associated with the presence of so-called hopping processes, i.e. types of movements in which the particle jumps abruptly to a site in the network which is about one interparticle distance away from the starting place [2]. These sort of processes are usually activated, since the jumping particle has to overcome a barrier formed by its surrounding particles (this is in contrast to the motion at higher temperatures, where the dynamics of the particles is smoother, i.e. where no jumps occur, see Fig. 2a). Thus the study of the van Hove correlation function shows us that the dynamics of the particles changes from a smooth movement to a jump-like motion when the temperature is lowered. It is this change in the microscopic dynamics that gives rise to the change in the temperature dependence of the diffusion constants.

A further important transport quantity is the shear viscosity η which can also be measured in real experiments. Unfortunately the calculation of η is not a simple task in computer simulations, since it is necessary to average this quantity over quite a few (at least 10) α -relaxation times (defined below) before η is determined with a reasonable accuracy. Therefore we were able to measure η only for temperatures larger than 3000 K. The temperature dependence of η is shown in Fig. 3 in an Arrhenius plot. Despite the noise in the data we can recognize that this temperature dependence is not Arrhenius like thus is similar to the temperature dependence of the diffusion constant. Also included in the figure are the experimental data points of the measurements of *Urbain et al.* [20]. We see that a reasonable extrapolation of our data to lower temperature will underestimate the viscosity at the temperatures at which the experimental values are available, which shows that with respect to this quantity the potential of van Beest *et al.* is perhaps not quite reliable. (However, it should also be kept in mind that the experimental data points might be subject to an appreciable systematic error.)

Since experimentally the viscosity is simpler to measure than the diffusion constant, it is often common to calculate the latter from the former by means of the so-called Eyring equation (which is essentially identical to the Stokes-Einstein equation), i.e.

$$D = k_B T / \eta \lambda. \quad (3)$$

Here k_B is Boltzmann's constant and the constant λ (having the dimension of length)

is related to the size of an elementary diffusion step and is usually determined from measurements at lower temperatures. Having measured both, D and η , we can now check whether the combination $k_B T / \eta D$ is indeed constant. This quantity is shown in the inset of Fig. 3 for the silicon as well as the oxygen diffusion constant. From this plot we clearly see that in the temperature range investigated the assumption that λ is constant is a poor approximation. It is, however, interesting that at the lowest temperatures the value of λ for the oxygen atoms is about 5\AA , which is not too different from 2.8\AA , the values assumed by *Poe et al.* [21] at lower temperatures.

The fact that the atoms of the system form a three dimensional open network implies that the bonds between adjacent atoms are broken if an atom diffuses. Therefore it is reasonable to look into the time dependence of these bonds. For this we define the quantity $P_b(t)$ which is the probability that a bond which is present at time $t = 0$ is also present at time t . (Note that we call a silicon and oxygen atom bonded if their distance is smaller than 2.35\AA , the location of the minimum between the nearest and second nearest neighbor peak in the Si-O radial distribution function. This location is essentially independent of temperature.)

In Fig. 4 we show the time dependence of P_b for all temperatures investigated. From this figure we recognize that at low temperatures the curves do not decay to zero within the time span of our simulation. From our investigation of the intermediate scattering function, discussed below, we know however, that this correlation function, which measures the structural relaxation of the system, does decay within the time span of our simulation. Thus we come to the conclusion that for the structural relaxation to occur it is not necessary that *all* Si-O bonds are broken, but only about 80% of them. This number is quite reasonable since it can be argued that an oxygen atom can make a relaxational movement if one or two of its bonds are broken and that a silicon atom can move if three of its bonds are broken, i.e. about 75% of the average number of bonds.

From Fig. 4 we also see that the shape of the curves is essentially independent of temperature (a *small* temperature dependence is observed for times at which P_b is still close to its initial value [10]). Thus we come to the conclusion that the mechanism that leads to the breaking of the bonds is also essentially independent of temperature. Thus it is reasonable to define the mean lifetime τ_b of a bond by requiring that $P_b(\tau_b) = e^{-1}$. This lifetime can now be compared with the typical time for the diffusion. For this we plot in Fig. 5 the products $D_{\text{Si}}\tau_b$ and $D_{\text{O}}\tau_b$ as a function of temperature. We recognize from this figure that this product is essentially constant for the oxygen atoms, but decreases for the

silicon atoms. Thus we conclude that the breaking of a bond is related to the diffusive movement of the oxygen atom, which is very reasonable, since this atom becomes mobile after the breaking of one of its bonds to its two nearest neighbors silicon atoms. For silicon atoms the situation is different: Even if one bond to its neighboring oxygen atoms is broken it is still tightly bound to the network by the remaining oxygen neighbors and thus cannot start to diffuse around. Therefore the quantity τ_b is not related to the diffusion constant of the silicon atoms and hence $\tau_b D_{\text{Si}}$ is not constant.

As mentioned above, the structural relaxation of the system can be studied very well by means of $F_s(q, t)$, the (incoherent) intermediate scattering function for wave-vector q . A further reason why this function is important is that it can be measured in neutron and light scattering experiments. It is defined as [17]

$$F_s^{(\alpha)}(q, t) = \frac{1}{N_\alpha} \left\langle \sum_{j=1}^{N_\alpha} \exp(iq \cdot (\vec{r}_j(t) - \vec{r}_j(0))) \right\rangle, \quad \alpha \in \{\text{Si}, \text{O}\} \quad . \quad (4)$$

In Fig. 6a we show the time dependence of $F_s^{(\text{O})}(q, t)$ for the wavevector $q = 1.7 \text{\AA}^{-1}$ which corresponds to the location of the first sharp diffraction peak in the static structure factor. We see that at high temperatures the curves decay quickly to zero with a time dependence which is approximated well by an exponential function. When the temperature is lowered a shoulder starts to form at around 0.4 ps which, upon lowering the temperature further, develops into a plateau. The time range during which the correlation function is close to the plateau is usually called the β -relaxation regime, whereas the time range during which the correlator starts to fall below the plateau and to zero is called the α -relaxation regime. The physical significance of this plateau is that in the time range where it is observed the particles rattle around in the cage formed by the neighboring particles and only for larger times this cage starts to break up, the particles begin to diffuse and thus the correlation function starts to decay to zero.

From Fig. 6a we also see that *at low* temperatures the shape of the curves seems, *in the α -relaxation regime*, to be independent of temperature. To check whether this is indeed the case we define the α -relaxation time $\tau(q)$ by requiring that $F_s(q, \tau(q)) = e^{-1}$. Thus, if the shape of the curves are in the α -relaxation regime indeed independent of temperature, a plot of the curves versus the *rescaled* time $t/\tau(q)$ should give a master curve. (If the correlation functions show such a scaling behavior one also says that they obey the *time-temperature superposition principle*.) That this is indeed the case is demonstrated in Fig. 6b, where we plot the same correlation function as shown in Fig. 6a versus $t/\tau(q)$. We see that we find indeed that the curves for the different temperatures fall, for low

temperatures, reasonably well onto a master curve. Thus we can conclude that the slowing down of the relaxation dynamics with decreasing temperature is *not* due to the fact that the decay of the correlation functions at long times becomes slower with decreasing temperature but rather that the time until the correlation functions start to deviate appreciably from the plateau, i.e. the time for the breaking up of a cage, increases strongly with decreasing temperature.

From Fig. 6 one also sees that at times around 0.2-0.5 ps the correlation functions for low temperatures show a noticeable dip. Such a feature is *not* observed in hard-sphere like systems, such as Lennard-Jones or soft spheres [2, 3, 22], which are fragile glassformers, and thus seem to be a particularity of strong glassformers. This dip is related to the so-called boson peak, a feature which has been observed in various experiments, such as inelastic neutron scattering, Raman scattering and more recently also in inelastic x-ray scattering. The reason for the presence of this peak is so far a matter of dispute [23] since the experiments are not able to provide the information necessary to decide between the different theoretical models. Thus this type of question might very well be one which will ultimately be decided by means of specific types of computer simulations, since those will allow to access the necessary information, and some efforts in this direction have indeed been made [24].

The last quantities we discuss in this article are the dispersion relations of the different modes. Within a computer simulation it is relatively simple to calculate the wave- and frequency dependence of the (collective) dynamic structure factors

$$S_{\alpha\beta}(q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F_{\alpha\beta}(q, t) \exp(i\omega t) dt \quad \alpha, \beta \in \{\text{Si}, \text{O}\} \quad , \quad (5)$$

with the coherent intermediate scattering functions

$$F_{\alpha\beta}(q, t) = \frac{N_{\text{Si}} + N_{\text{O}}}{N_{\alpha} N_{\beta}} \int d\vec{r} \exp(-i\vec{q} \cdot \vec{r}) \left\langle \sum_{k=1}^{N_{\alpha}} \sum_{j=1}^{N_{\beta}} \delta(r - |\vec{r}_j(t) - \vec{r}_k(0)|) \right\rangle, \quad (6)$$

since all the necessary information to compute this quantity is readily accessible. The dynamic structure factors are interesting for at least two reasons: Firstly they can be also measured in experiments, although only in a relatively limited range of frequency and wave-vectors, and secondly they allow insight into the nature of the excitations present in the system, such as the acoustic modes and the optical modes. The fact that we can compare the results of $S_{\alpha\beta}(q, \omega)$ from a simulation with real experimental data gives us the possibility to test whether the silica model used is able to reproduce this type of dynamic

observable in a satisfactory way. In the case where such a comparison is satisfactory we then can thus use the results from the simulation to gain information on $S_{\alpha\beta}(q, \omega)$ in those q and ω ranges which are not accessible to real experiments. Such comparisons have indeed been made and it was shown that the present models for silica agree quite reasonably with experiments [10, 24].

Once the spectra are obtained as a function of frequency the location of the various peaks can be read off and thus the dispersion relation of the different modes determined. (Note that for the investigation of the q -dependence of the *transversal* modes it is necessary to compute the transversal current-current correlation function $C_t(q, \omega)$, which can also be expressed simply by means of the positions and velocities of the particles [17].)

In Fig. 7 we show the so obtained dispersion relations for the different modes at 2900 K [9, 10]. The data for the Si-Si and the O-O correlation are shown in filled and open symbols, respectively. Starting at small wavevectors, various branches can be observed for each species: Two optical ones in the transverse and longitudinal modes, denoted by LO1, LO2, TO1 and TO2, and a longitudinal and transversal acoustic mode (LA and TA, respectively). In addition to these modes we find at wavevectors larger than 0.22\AA^{-1} an *additional* peak in the dynamic structure factor at around 2THz (see Fig. 7b). From its location at higher values of q , which is always around 2THz and a comparison with experimental data [25, 26], we conclude that this excitation is the so-called boson peak. The wavevector dependence of the different modes becomes relatively complicated when q is large and it has been discussed in greater detail in Refs. [27]. E.g. we see that the longitudinal acoustic mode for the silicon atoms (open triangles pointing downwards) show a quasiperiodic q -dependence which reflects the fact that the system has a pseudo-Brillouin zone at around 1.4\AA^{-1} [27]. Presently we do not want to dwell further on the discussion of the various curves and just point out one last thing. In Fig. 7b we have also included two bold solid lines. These present the linear dispersion behavior of the acoustic modes in the viscoelastic limit. Note that the slopes of the lines, which is equal to c_L and c_T , the longitudinal and transversal speed of sound, were *not* taken as a fit parameter, but are the experimental speeds of sound at around 1600 K [26]. From the fact that for small wavevectors our data points lie very well on (in the case of the longitudinal mode) or at least quite close (in the case of the transversal mode) to these lines with the experimental slopes we conclude that our simulations are able to reproduce also this type of measurements with good accuracy.

Conclusions

The goal of this review was not to make a comprehensive review of all the computer simulations of supercooled liquids and glasses. Rather we tried to present some exemplary results in order to demonstrate how computer simulations can contribute to our understanding of the dynamics of supercooled liquids. As already mentioned in the Introduction, the most valuable use of computer simulations is *presently* not to try to reproduce the dynamical features of the material of interest to a *very* high accuracy. Rather it is advisable to use rather simple models which are able to reproduce the *essential* features that one is interested in and to make a careful investigation of the properties of such models. As we have demonstrated in this article, even such relatively simple models can give a quite realistic description of reality. Due to their simplicity, however, it is possible to simulate system sizes and time scales that would not be accessible with more sophisticated models. Because with today's computer hardware it is possible to simulate systems that are reasonably large, on the order of 50\AA , for time spans (10-50 ns) that are much longer than the microscopic times (1 ps), such simulations can indeed give valuable information into the dynamics of glass melts and glasses, such as the lifetime of a bond, the mechanism of diffusion or the dynamics of the particles on the microscopic scale, quantities that are experimentally accessible only in a limited way, or not at all. Therefore these types of computer simulations are a valuable complement to experimental investigations to understand the dynamics of such systems.

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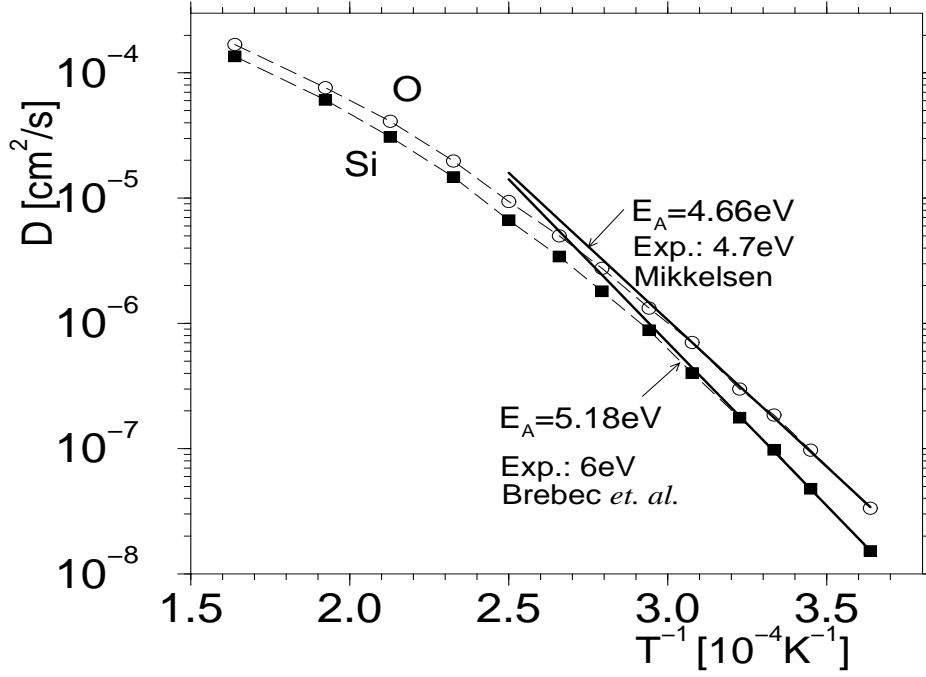
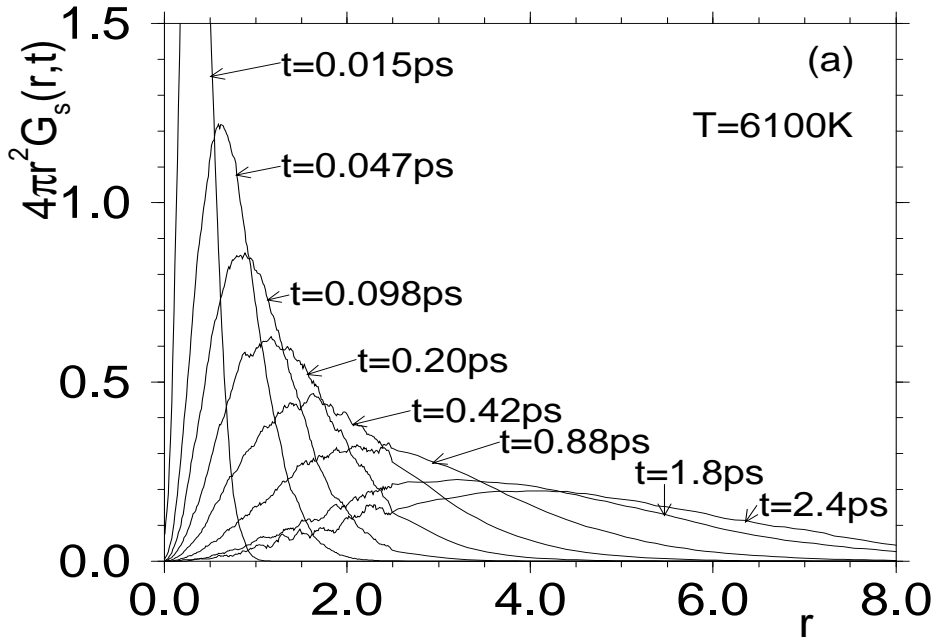


Figure 1: Temperature dependence of the diffusion constant for the silicon and oxygen atoms (filled squares and open circles, respectively). The straight lines are fits to the low temperature data with an Arrhenius law giving the stated activation energies. The experimental values for the activation energies (from Refs. [15] and [16]) are also given. Adapted from Ref. [8].



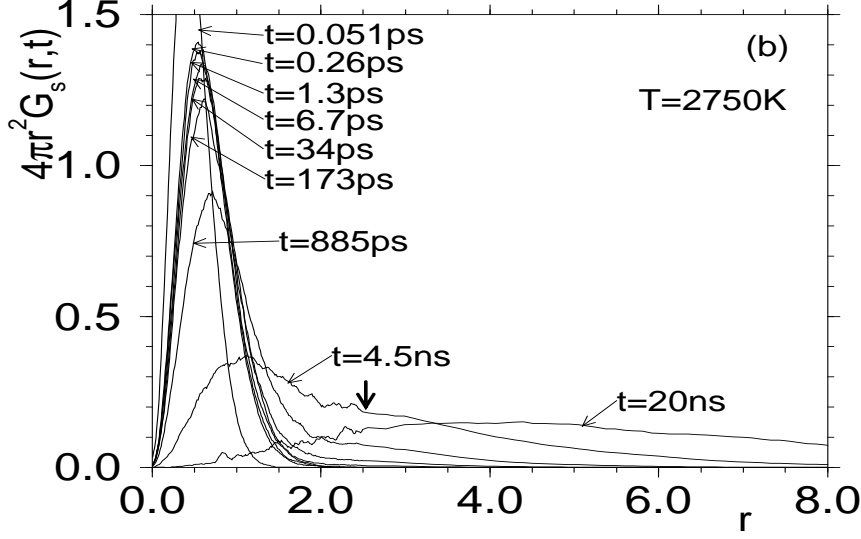


Figure 2: The self part of the van Hove correlation function for the oxygen atoms versus distance r for times that are evenly spaced on a logarithmic time axis (see labels). a) $T = 6100$ K, b) $T = 2750$ K. The arrow marks the location of the secondary peak. From Ref. [10].

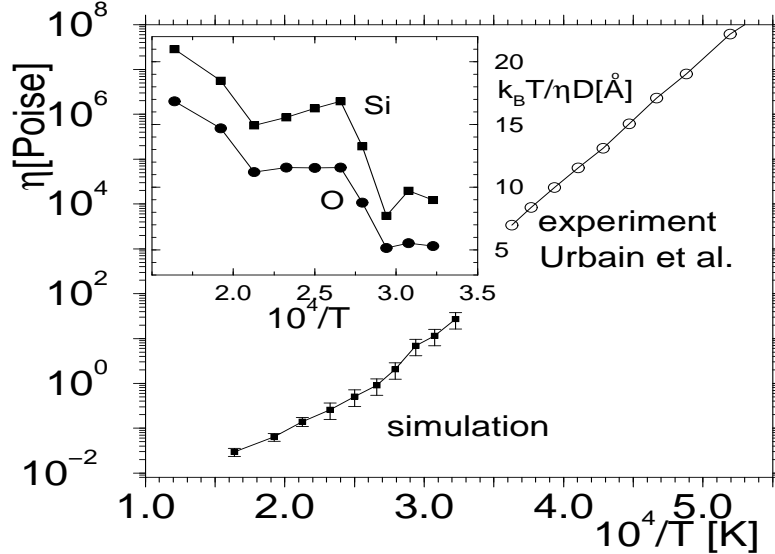


Figure 3: Main figure: Temperature dependence of the viscosity as determined from the simulation, (filled squares), and from the experiments of *Urbain et al.*, (open circles) Ref. [20]. Inset: Temperature dependence of $k_B T / D \eta$ for the silicon and oxygen diffusion constant (circles and squares, respectively). From Ref. [10].

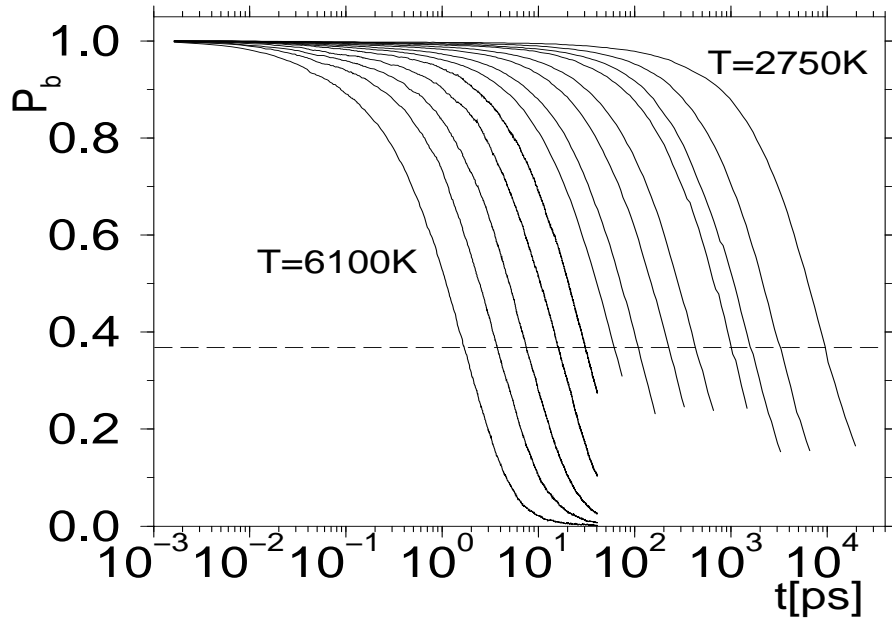


Figure 4: Time dependence of $P_b(t)$, the probability that a Si–O bond which was present at time $t = 0$ is also present at time t , for all temperatures investigated. The horizontal dashed line at e^{-1} is used to define the lifetime τ_b of a bond. From Ref. [10].

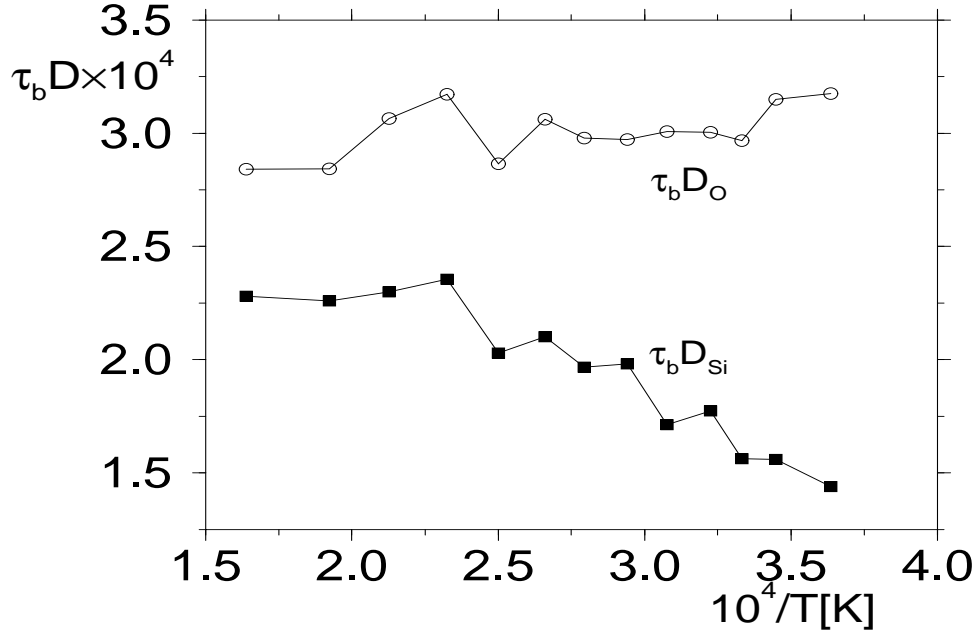


Figure 5: Temperature dependence of the product between the lifetime of a Si–O bond and the silicon and oxygen diffusion constant (filled and open symbols, respectively). From Ref. [10].

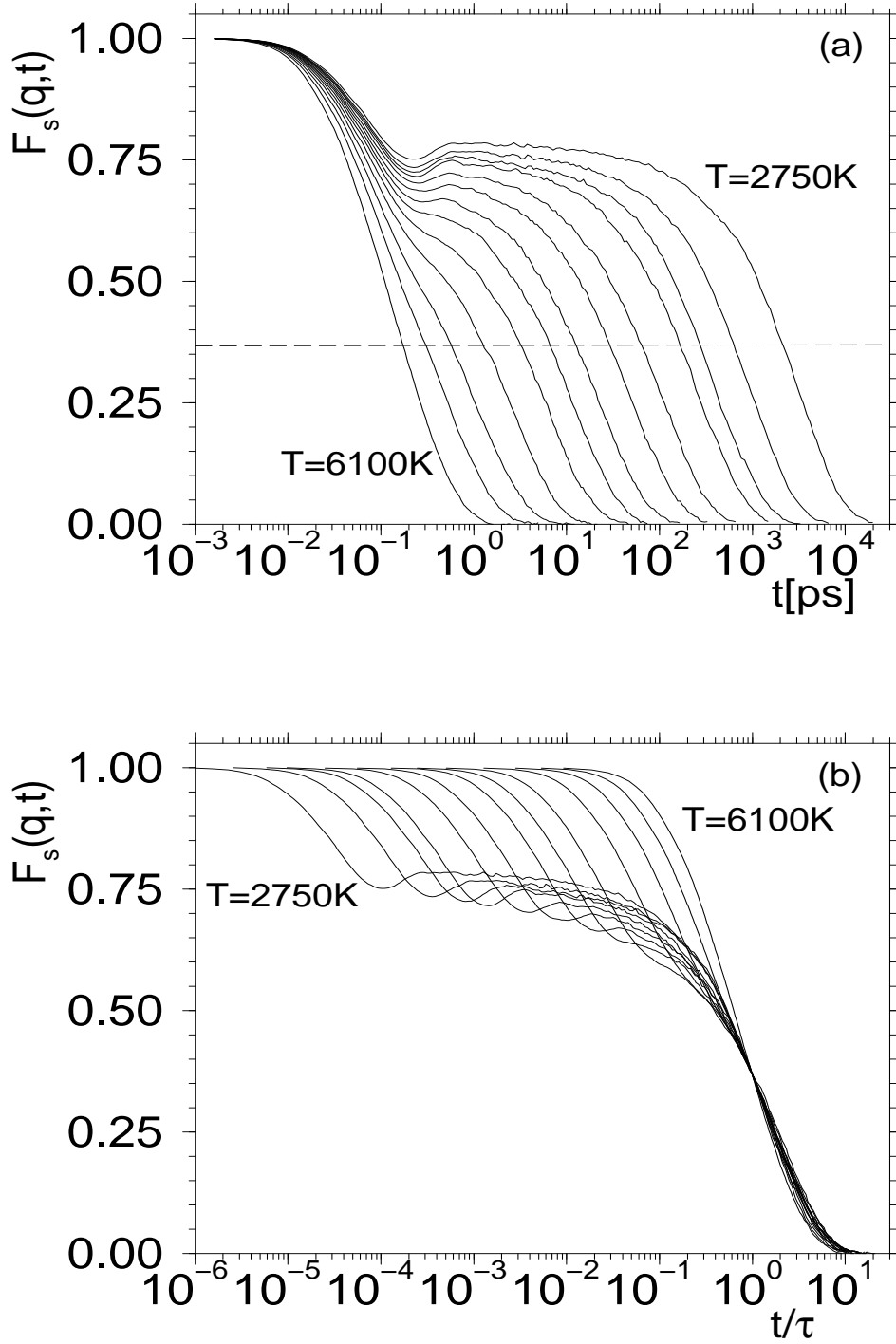


Figure 6: a) Time dependence of the incoherent intermediate scattering function $F_s(q, t)$ for the oxygen atoms for all temperatures investigated. The value of the wavevector q is 1.7\AA^{-1} and corresponds to the location of the first sharp diffraction peak in the static structure factor. The horizontal dashed line at e^{-1} is used to define the α -relaxation time τ . b) Same data as in a) but plotted versus the rescaled time $t/\tau(T)$. From Ref. [8].

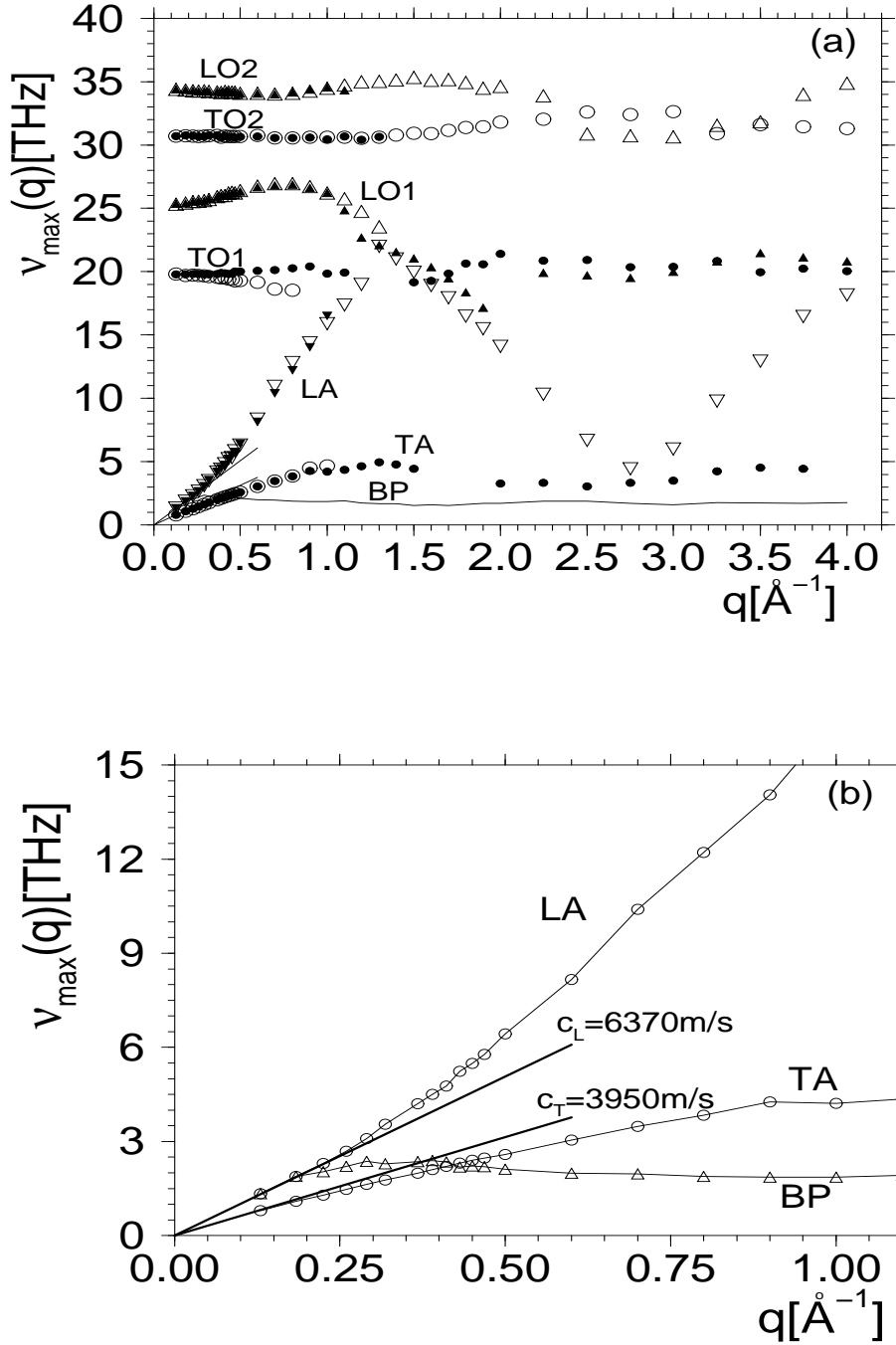


Figure 7: Dispersion relations for different modes at $T = 2900 \text{ K}$. The filled and open symbols correspond to the Si-Si and O-O correlation, respectively. The first character in the labels (L,T) stands for longitudinal and transversal and the second character (O,A) for optical and acoustic. The dispersion relation labeled BP is the one for the boson peak. a) All wavevectors considered. b) Dispersion relations at small wavevectors for the O-O correlation. The two straight lines are the expected dispersion relation if the experimental velocities of sound are assumed [26]. Adapted from Ref. [10].